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To cite this article: H Judawisastra *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **223** 012066

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## Water absorption and its effect on the tensile properties of tapioca starch/polyvinyl alcohol bioplastics

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**Abstract.** Tapioca is one of the largest sources of starch and makes it suitable to be used for bioplastic material. Addition of polyvinyl alcohol (PVA) has been shown to successfully reduce the brittleness of starch bioplastic. This study aims to investigate the influence of PVA addition to water absorption behavior and its effect on the tensile properties of tapioca starch/PVA bioplastics, which are still not yet fully understood until now. The bioplastics were prepared by solution casting method at gelatinization temperature, with PVA addition from 0 to 29 wt%. Examinations were carried out by means of water absorption test, tensile test and Fourier Transform Infrared (FTIR) Spectroscopy. Increasing content of PVA, up to 29 wt%, was found to decrease the water absorption of the bioplastics, with the lowest water saturation point of 251%. This is due to the interaction between starch and PVA which reduces the free OH groups in the resulting bioplastics. Consequently, this led to a decrease in water absorption-related deterioration, i.e. tensile properties degradation of the bioplastics. The addition of 29 wt% resulted into the lowest degradation in tensile strength (6%) and stiffness (30%), while accompanied with the highest elongation increase (39%) after water immersion.

### 1. Introduction

There has been a growing interest in the application of bioplastics, which are plastics material that are either biobased, derived from biomass; biodegradable; or features both properties [1]. This is mainly driven by the major issues involved in the use of conventional petrochemical plastic that are non-biodegradable and ultimately result into several environmental problems. Starch-based plastics are one type of bioplastics that are both biobased and biodegradable. The raw material for this type of plastics is sustainable and abundant, and thus make them a promising candidate as an alternative to conventional plastics. Starch can be found in the seeds, leaves, fruits, stems, roots, and tubers of most plants, such as maize, rice (paddy), wheat, potatoes, cassava, bananas, yams, and sorghum [2].

Despite the growing interest in bioplastics, the use of starch-based plastic is still limited due to its brittleness and moisture sensitivity when compared to conventional synthetic plastics [3]. The hydrophilic nature of starch makes the plastic based on this material have a poor long-term stability and its mechanical properties are sensitive to moisture [1, 3]. One strategy that has been demonstrated to improve starch-based plastic performance is by adding polyvinyl alcohol (PVA). PVA is a water-soluble synthetic polymer that is made from petrochemicals, and hence is biodegradable [4]. Therefore, the blends composed of PVA and starch are biodegradable. The addition of PVA is of



particular interest, since it has been shown to have an excellent compatibility with starch [5], and in fact has successfully reduced the brittleness and the water uptake of starch-based plastics [6].

Tapioca (cassava) is one of the largest source of starch, particularly in tropical environments [2]. This type of plant is abundantly available in Indonesia as it is one of the main food crops in the country. Hence, it is believed that tapioca has a great potential to be used for bioplastic material. Several studies on this topic have been carried out for the past years, i.e. to develop plastic foams [7], edible films [8], and thermoplastic starch [9]. To present, however, the effect of water absorption in tapioca starch/PVA bioplastic, particularly to its tensile properties degradation, is still not yet fully understood. Therefore, this study aims to investigate the influence of PVA addition to water absorption behavior and its effect on the tensile properties of tapioca starch/polyvinyl alcohol bioplastics.

## **2. Research Methodology**

### *2.1. Materials*

A commercially available tapioca starch, trade name Gunung Agung supplied by PT. Budi Acid Jaya Tbk., was used in this study. The polyvinyl alcohol (PVA) polymers used were purchased from Central Kimia, Bandung. High water content was used to produce starch-based bioplastic film.

### *2.2. Bioplastic Film Preparation*

The bioplastic films were prepared by solution casting method, with PVA addition at different concentrations of 0 (starch reference material), 17 and 29 wt%. Pure PVA was also investigated as PVA reference material. The weight percentages of PVA were calculated with respect to the total weight of dry starch and PVA. The sample nomenclature is referenced according to the tapioca starch (TS) and PVA contents, i.e. TS/PVA x/y for a film with x wt% TS and y wt% PVA. All films were made with constant amount of water and dry tapioca starch, i.e. 140 g and 10 g, respectively. PVA was first added into a beaker containing water. The mixture was then stirred with a magnetic stirring bar and heated to 85°C. Once the desired temperature of 85°C was reached, the mixture was immediately cooled down to 40°C using a cooling fan. Tapioca starch was then added to the mixture, stirred and heated in a water bath to the gelatinization temperature of 68°C. Once the gelatinization temperature was reached, the blend was cast onto the aluminium mould and let dried at room temperature for about 1 to 2 days.

### *2.3. Water Absorption Tests*

Water absorption tests were performed on the samples following ASTM D570-98 with modification, i.e. immersion method in distilled water at 21.5°C for the duration up to 60 min. The samples were

taken out periodically at different intervals, i.e. at 1, 3, 5, 10, 15, 20, 25, 30, and 60 min. After being taken out from the water, all of the samples were weighed immediately after wiping out the water on the surface of the sample. The amount of water absorbed was determined by calculating the weight gain after immersion to the nearest 0.0001 g.

#### 2.4. Bioplastic Film Characterizations

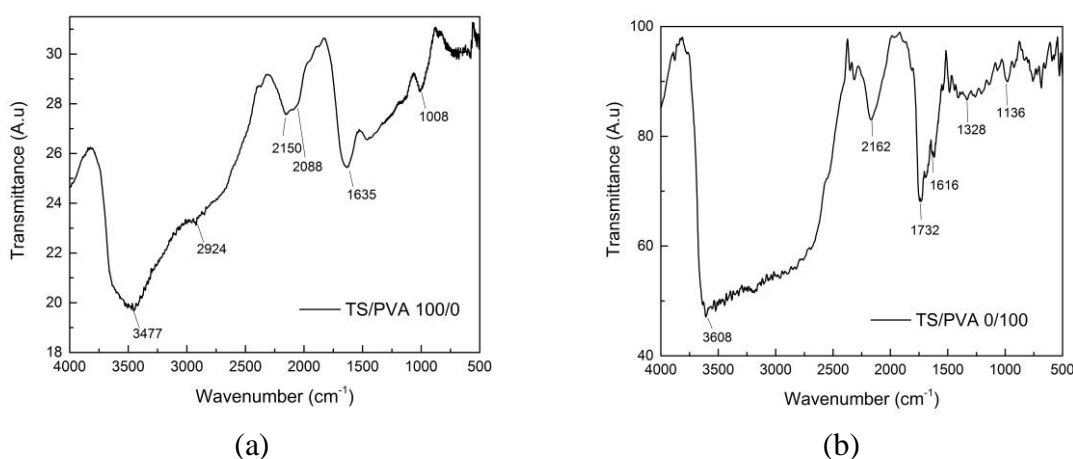
Chemical structure of the bioplastics was characterized by Fourier Transform Infrared (FTIR) Spectroscopy in order to examine the mixing of the tapioca starch and PVA, and the effect of water absorption. The FTIR characterizations both before and after water immersion, with the samples in dry condition, were carried out in order to investigate the effect of water absorption.

Tensile tests were carried out according to ASTM D-882-02 for thin film with a thickness of 0.1 mm. Tensile properties were measured using a Tensilon RTF-1310 equipped with a 1 kN load cell, with a 10 cm gage length at a crosshead speed of 5 mm/min. Two replicates of the samples before and after water immersion were tested in dry condition for each type of material and the average value was reported. The wet samples after immersion were first dried using cooling fan prior to the tensile test. The samples were dried until the initial weight before water immersion was reached.

### 3. Results and Discussion

#### 3.1. Tapioca Starch/Polyvinyl Alcohol Bioplastics Chemical Structure Analysis

FTIR characterization results of the pure tapioca starch (TS) and pure polyvinyl alcohol (PVA) bioplastics are shown in Figure 1a and b, respectively. Functional groups assignment of TS and PVA has been reported in many other studies [10-13].



**Figure 1.** FTIR spectra of: (a) pure tapioca starch (TS) and (b) pure polyvinyl alcohol (PVA) bioplastic reference materials.

The characteristic peaks assignment for the pure TS and pure PVA are summarized in Table 1. Compared with those already reported by other research groups [10-13], some differences are evident

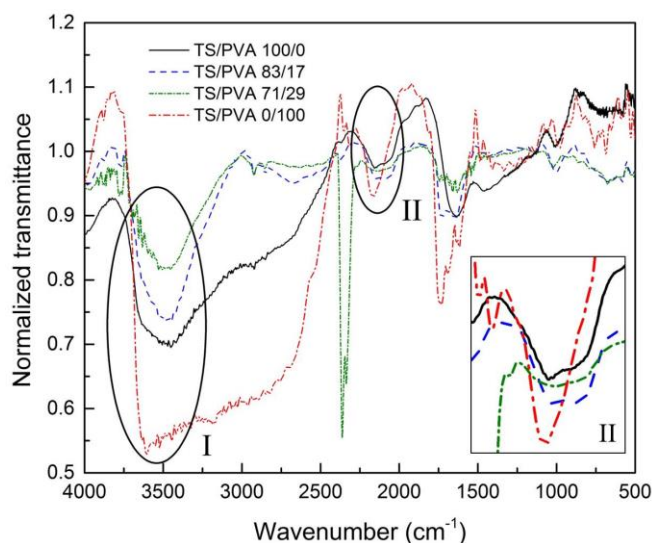
from the FTIR result in the present work. In the pure TS, peaks at 2150 and 2088  $\text{cm}^{-1}$ , were not evident in the other reported studies [10, 11]. Those peaks are indicators for combination of O-H stretching vibration that represent the degree of hydrogen bonding in TS. The adjacent peaks to the peaks at 2150 and 2088  $\text{cm}^{-1}$  indicate that there are hydrogen bonds among amylose chains, and between amylose and amylopectin.

In the pure PVA, peak at 2162  $\text{cm}^{-1}$  were not evident in the other reported study on PVA [12, 13]. This is again the peak which is indicator for combination of O-H stretching vibration. The single peak in PVA indicates that the hydrogen bonds are only formed among PVA chains. Further, the peak at 3000 - 2800  $\text{cm}^{-1}$ , which is assigned for C-H stretching of  $\text{CH}_2$  [12, 13], was not obviously seen in the FTIR spectra of pure PVA (see Figure 1b). This may occur due to the presence of water in the pure PVA sample which then makes the broad O-H stretching peaks to overlap with the C-H stretching peak.

**Table 1.** FTIR assignment of pure tapioca starch and pure polyvinyl alcohol bioplastic reference materials

Assignment	Tapioca starch	Polyvinyl alcohol
O-H stretching	3477 $\text{cm}^{-1}$ (broad)	3608 $\text{cm}^{-1}$ (broad)
C-H stretching of $\text{CH}_2$	2924 $\text{cm}^{-1}$	-
Combination of O-H stretching	2150 and 2088 $\text{cm}^{-1}$	2162 $\text{cm}^{-1}$
C=O stretching of PVA residue	-	1732 and 1616 $\text{cm}^{-1}$
O-H bending	1635 $\text{cm}^{-1}$	-
C-H wagging of $\text{CH}_2$	-	1328 $\text{cm}^{-1}$
C-O stretching	1008 $\text{cm}^{-1}$	1136 $\text{cm}^{-1}$

Figure 2 presents the Fourier transform infrared spectroscopy (FTIR) spectroscopy characterization result for all tapioca starch/polyvinyl alcohol (TS/PVA) bioplastics. Pure TS and pure PVA reference materials are added for comparison. There are two regions of interest shown in Figure 2 i.e. the first region (I), broad peaks in the range 3500 to 3400  $\text{cm}^{-1}$ , which are assigned for O-H stretching vibration, and the second region (II), from 2200 to 2000  $\text{cm}^{-1}$ , where the O-H stretching combination peak can be found.



**Figure 2.** Combined FTIR spectra of pure tapioca starch (TS/PVA 100/0), pure polyvinyl alcohol (TS/PVA 0/100) and tapioca starch/polyvinyl alcohol bioplastics

It can be seen from region I that the highest O-H stretching peak can be found in the pure PVA and immediately followed by pure TS. The addition of PVA appears to reduce the amount of O-H bonds in the pure TS, which indicates that free OH groups in the pure TS are forming hydrogen bonds with the OH groups in the pure PVA. The increasing amount of hydrogen bonding between TS and PVA leads to the decrease in the detected amount of O-H stretching.

The O-H stretching combination found in region II represents the degree of hydrogen bonding in the samples. There are two adjacent peaks at 2150 and 2088  $\text{cm}^{-1}$  in the pure TS, while in the pure PVA, there is one peak at 2162  $\text{cm}^{-1}$  (see Figure 2). In the bioplastics with the addition of 17 and 29 wt% PVA, there exists two adjacent peaks, i.e. at 2146 and 2073  $\text{cm}^{-1}$ , and at 2135 and 2071  $\text{cm}^{-1}$ , respectively. Note that the peak at 2017  $\text{cm}^{-1}$  in the higher amount of PVA, at 29 wt%, is not as evident as the peak at 2073  $\text{cm}^{-1}$  seen in the 17 wt% PVA sample. This shows that the amount of peaks in the resulting bioplastics gets more closely resemble that of the pure PVA with the addition of PVA. Therefore, the observations in region I and II (as shown in Figure 2) confirms the formation of bonds between PVA and tapioca starch.

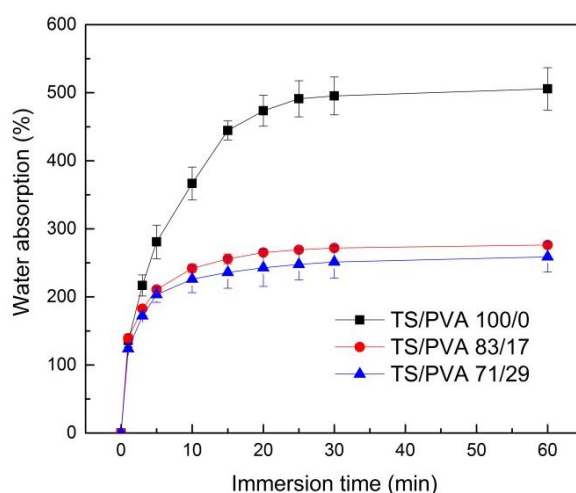
### 3.2. Water Absorption Behaviour

Figure 3 shows the amount of water absorbed by the bioplastic film samples at three different PVA contents. All of the films absorbed water very rapidly during the initial stage and later gradually level off reaching the saturation level after around 30 min of immersion. The pure TS film showed higher water absorption compared to the TS/PVA films. Water absorption increased with increasing immersion time, but decreased with increasing PVA content, with the lowest water saturation point of 251% from the addition of 29 wt% PVA. This is similar to the behavior seen in another starch blend

films, i.e. polyvinyl alcohol/corn starch blends [14]. The starch is mainly responsible for the water absorption of the blends due to its inherent hydrophilic nature.

A general rule of mixtures can be used to explain the decrease of water absorption with increasing PVA content. The rule is that the final properties of a blend consisted of two or more polymers are a weighted mean of the material constituents' properties. The tapioca starch reference material has been shown to have a maximum water absorption of 495% (see Figure 3, TS/PVA 100/0), while PVA has been reported to have a maximum of 43% [14]. The addition of 17 and 29 wt% PVA resulted into water saturation point of 271% and 251%, respectively. These values are in fact still in the range between the saturation points of each pure material constituent.

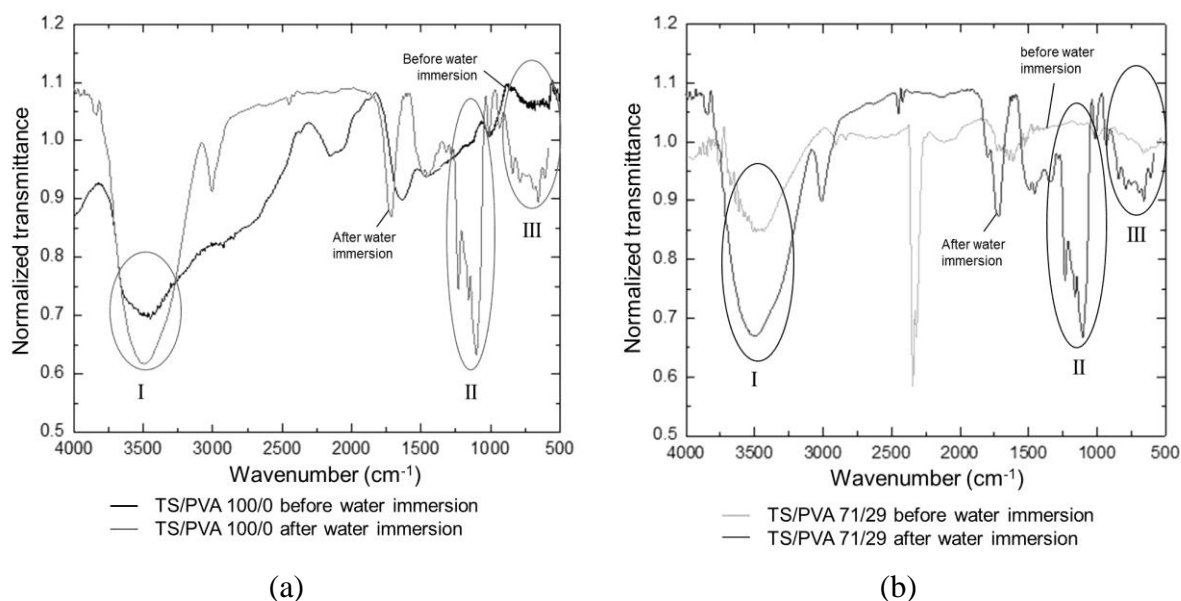
As previously shown in the FTIR result in section 3.1. the interaction between PVA and TS leads to the decrease of free OH groups in the TS/PVA bioplastics. This will ultimately make the resulting TS/PVA bioplastics become less hydrophilic, hence less sensitive to the presence of water.



**Figure 3.** Water absorption of tapioca starch/ polyvinyl alcohol (TS/PVA) bioplastics.

### 3.3. Fourier Transform Infrared Spectroscopy (FTIR) Spectroscopy Analysis after Water Absorption

Figure 4 presents the FTIR characterization results for pure TS (see Figure 4a) and TS/PVA (see Figure 4b) bioplastics in two conditions: before and after water immersion. There are four regions of interest which show the influence of water absorption on the chemical structure of the bioplastics. A similar tendency of the influence of water absorption was observed for both the pure TS and TS/PVA bioplastics.



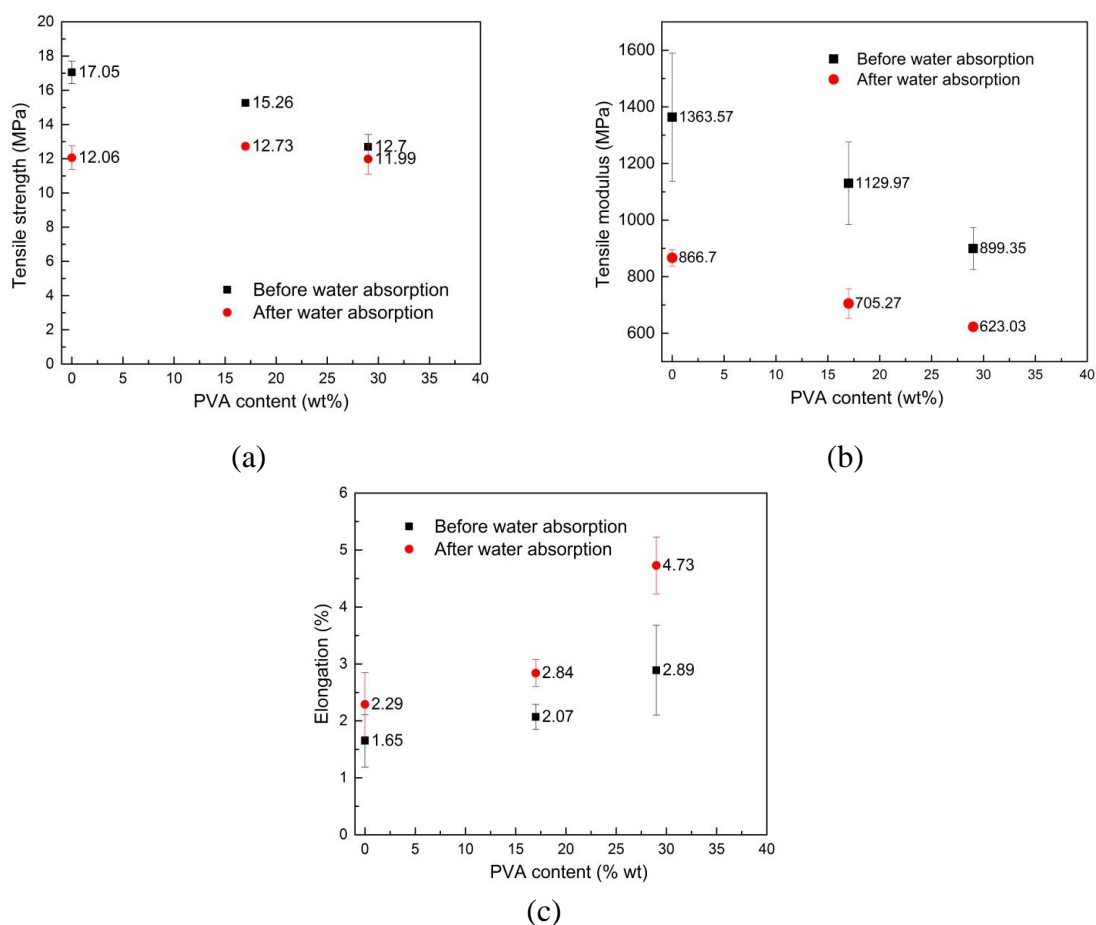
**Figure 4.** Effect of water absorption on the chemical structure of tapioca starch/ polyvinyl alcohol (TS/PVA) bioplastics samples (tested in dry condition).

The observation in the three regions indicates that hydrolysis of starch occurs due to the interaction with water. After water immersion, the O-H stretching peak, broad peak in the range from 3500 to 3000 cm<sup>-1</sup> (see region I), became stronger. Further, strong peaks from 1300 to 1000 cm<sup>-1</sup> (see region II) and around 840 and 915 cm<sup>-1</sup> (see region III) became evident after water immersion. The strong peaks in region II are assigned for C-O stretching, while the strong peaks in region III are characteristic for  $\alpha$ -D glucose. After water absorption, hydrolysis may occur in the bioplastics when water attacks C-O-C bonds in starch and forms O-H bonds, leading to the breaking down of starch into smaller chains and hence degrades the tapioca starch [15]. As indicated in the FTIR result, the breaking down of C-O-C bonds in starch leads to the formation of C-O bonds and  $\alpha$ -D glucose monomers. This degradation in starch chemical structure may ultimately affect the tensile properties of the bioplastics, as will be shown later in the following section.

### 3.4. Effect of Water Absorption on Tensile Properties of Tapioca Starch/Polyvinyl Alcohol Bioplastics

Figure 5 shows how the tensile properties of the tapioca starch/polyvinyl alcohol bioplastics are affected by water absorption. When looking at each tensile property individually, the tensile strength after water absorption appears to be similar for all types of TS/PVA bioplastics. On the other hand, the tendency in the change of both the tensile stiffness and elongation after water absorption were still similar with that of before water absorption. After water absorption, the bioplastics with 29 wt% PVA still have a lower stiffness but with a higher elongation compared to the ones with lower PVA content.





**Figure 5.** Effect of water absorption on the tensile properties of tapioca starch/ polyvinyl alcohol bioplastics: (a) tensile strength, (b) stiffness and (c) elongation.

It is immediately clear from Figure 5a and b that the absorbed water degrades the tensile strength and stiffness of the bioplastics. Increasing PVA content up to 29 wt% appears to decrease the tensile strength and stiffness degradation which occurs after water immersion. The lowest degradation in tensile strength and stiffness of 6% and 30%, respectively, were observed at the highest PVA addition (29 wt%). On the other hand, Figure 5c shows that the absorbed water increases the elongation. Increasing PVA content leads to a higher elongation increase which occurs after water immersion. The highest increase in elongation of 39% (compared to the dry condition) was also observed at 29 wt%. This reduction in brittleness after water absorption is particularly advantageous for bioplastics application, for example as packaging material, in aqueous environment.

From the observations in Figure 5, it can be concluded that the addition of PVA to TS bioplastics leads to a better tensile strength and stiffness retention, and a higher elongation increase after water immersion. This may be attributed to the reduction of water absorption by the bioplastics with PVA addition, which was caused by the less hydrophilicity of these bioplastics, as confirmed in

the previous data (see section 3.2. ). The reduction in absorbed water then leads to a decrease in the amount of hydrolyzed bioplastic polymer chains.

#### 4. Conclusion

Tapioca starch/polyvinyl alcohol bioplastics were made with the addition of PVA from 0 to 29 wt%. Increasing content of PVA was found to decrease the water absorption of the bioplastics, with the lowest water saturation point of 251% observed at the highest PVA addition (29 wt%). This is due to the interaction between the starch and PVA which reduces the free OH groups in the resulting bioplastics. Consequently, this also led to a decrease in water absorption-related deterioration, where a better retention of tensile strength and stiffness, and a higher elongation increase after water immersion was found. The addition of 29 wt% resulted into the lowest degradation in tensile strength (6%) and stiffness (30%), while accompanied with the highest elongation increase (39%) after water immersion.

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